

The Role of Interparticle Connection and SEI Layers on Capacity Fade in Lithium-Tin Alloy Electrodes

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Lithium alloys (aluminum and silicon) have been cycled as negative electrodes with molten salt electrolytes at 400 °C for over a thousand deep cycles with little capacity fade.¹ However, when lithium alloys are used with organic electrolytes at room temperature, rapid capacity fade occurs. What is the difference between these two situations? Temperature would affect the diffusivity of lithium in the alloy, but solid diffusion resistance cannot fully explain the loss of capacity. Therefore, the interaction between the alloy and the electrolyte must be responsible for the difference in performance.

Before one can design an alloy electrode with better capacity retention, one must understand what mechanisms cause the loss of capacity, and how different electrode designs would address these failure mechanisms. Numerous studies have stated that the volume change during phase change is responsible for the capacity fade of alloy electrodes. But how exactly does volume change cause loss of capacity? We will present the results of experiments to test the following hypothesis for a failure mechanism (see figure 1). Upon lithiation, particles expand, creating new surface area and causing some particle fracture as the particles push against each other. If the electrolyte is not stable at the potential range of lithiation, a solid-electrolyte interphase (SEI) layer will grow on all exposed surfaces. When the current is reversed and delithiation occurs, the particles contract. We hypothesize that this contraction may lead to loss of capacity for two reasons: first, because an insulating SEI layer may grow between the particles during the change in volume, and second, because the particles may contract away from each other, interrupting the path of electrons to the current collector. By this hypothesis, capacity fade in alloy electrodes can be reduced only by designs which force the particles to stay connected during delithiation and which prevent the SEI layer from forming between particles. Of course, the design also will have to prevent agglomeration, another failure mechanism, which leads to increase of solid diffusion resistance.

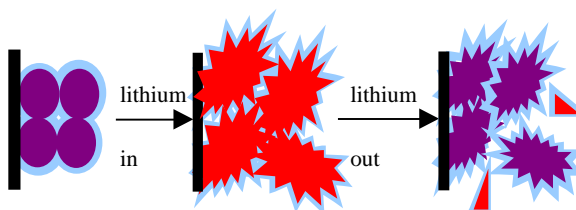


Figure 1: Proposed mechanism for loss of electrical contact among alloy particles (dark grey) covered by an SEI layer (light grey). Some particles may fracture upon lithiation into pieces which, upon delithiation, contract away from a continuous path to the current collector, while particles simultaneously may become disconnected if a resistive SEI layer grows in between them.

We test our hypothesis by comparing the rate of capacity fade and the change in resistance of tin electrodes cycled with the commonly-used electrolyte, LiPF_6 in ethylene carbonate/dimethyl carbonate, which is known to be unstable at the potential of lithiated tin, to the performance in ether electrolytes such as poly(ethylene glycol)-dimethyl ether, which are more stable at low potentials. One would expect that electrolytes which are less thermodynamically stable would react to form a more resistive SEI layer. In addition, we examine the effect of washing a cycled electrode to remove the SEI layer and then cycling the washed and reformed electrode. Electrodes were fabricated from 12 μm diameter tin powder (Aldrich) with 10 wt% poly(vinylidene fluoride) doctor-bladed onto copper foil. Finally, we discuss how different design options impact these failure mechanisms.

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REFERENCE

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